PROCESS DESIGN AND CHEMISTRY
OF THE
NOXSO PILOT PLANT DEMONSTRATION

Rita E. Bolli, John L. Haslbeck[1], B. Dwight Coffin[2], and L. G. Neill[1]

Ohio Edison Company
Environmental and Special Projects Dept.
76 South Main Street
Akron, OH 44308

[1]NOXSO Corporation, Library, PA
[2]MK-Ferguson Company, Cleveland, OH

Key Words: NOXSO, FGT (flue gas treatment), pollution (control technology).

ABSTRACT

Ohio Edison Company, NOXSO Corporation, MK-Ferguson, and W. R. Grace Co. are conducting a Proof-of-Concept (POC) test of the NOXSO flue gas treatment system at Ohio Edison's Toronto Plant in Toronto, Ohio. The project is co-funded by the U.S. Department of Energy's (DOE) Pittsburgh Energy Technology Center (PETC), the Ohio Coal Development Office and the project team. The pilot plant treats flue gas from either Boiler No. 10 or No. 11 at Toronto containing approximately 2300 ppm SO_2 and 350 ppm NO_x. The pilot plant treats a volume of flue gas equivalent to 5 MW of power production, which makes the pilot plant roughly 1/20 the size of a commercial process module. This paper presents the design and process chemistry of the pilot test facility.

Background

On May 10, 1989, a consortium consisting of Ohio Edison, NOXSO Corporation, MK-Ferguson, and W. R. Grace Co. signed a cost-shared contract with the DOE/PETC to conduct a Proof-of-Concept (POC) test of the NOXSO process. The POC project will take approximately three years to complete, and the test will be conducted at Ohio Edison's Toronto Plant at Toronto, Ohio.

POC Test Site

The POC unit will treat flue gas from either Boiler No. 10 or No. 11 at Ohio Edison's Toronto Plant. Two sources of flue gas will be tapped so that the POC test can continue as long as one of the boilers is operating. A slipstream of flue gas will be taken from either boiler in the amount of 12,000 SCFM. The slipstream will be taken downstream of the Toronto Plant's electrostatic precipitators (ESPs) which remove 99 percent of the particulate matter from the flue gas. The Toronto boilers are pc-fired and burn Ohio coal containing 3.7 percent sulfur. The flue gas typically contains 2300 ppm SO_2 and 350 ppm NO_x.

POC Test Schedule

Detailed design engineering has been completed and the major pieces of equipment have been ordered. Construction began in March 1990 and will be completed in November 1990. The test is scheduled to begin in January 1991 and will run through August 1991.

POC Process Flow Diagram

The process flow diagram for the POC is shown in Figure 1. The system is best described by following the flow of flue gas, sorbent, and regeneration gas through the process.

Flue gas will be available from either Boiler No. 10 or No. 11 at the Toronto facility and will be taken downstream of the respective ESP. The base case condition will treat 12,000 SCFM of flue gas, equivalent to approximately 5 MWe. The flue gas, once past the ESP, will enter the NOXSO flue gas treatment system. The flue gas first passes through the adsorber feed blower and then is cooled by vaporizing a water stream sprayed directly into the duct work. The cooled flue gas then passes through the fluidized bed adsorber where SO_2 and NO_x are simultaneously removed. The clean flue gas then enters a cyclone that returns entrained sorbent larger than 20 microns back to the adsorber fluid bed. Attrited sorbent smaller than 20 microns diameter will pass through the cyclone along with any flyash remaining in the flue gas, and the entire stream will pass through a baghouse for final particulate removal.

After the sorbent is to loaded with SO_2 and NO_x, it is removed from the adsorber and feeds the dense phase pneumatic conveying system. Fresh make-up sorbent is also added to the dense phase conveying system from the make-up sorbent bin. Compressed air is then used to lift the sorbent to the sorbent heater. The sorbent passes through a disengaging chamber where the lift air is separated from the sorbent. The sorbent heater is a three-stage fluidized bed where a hot air stream is passed countercurrent through the sorbent raising the sorbent temperature from the adsorber temperature of 250°F to the regeneration temperature of 1220°F. During the heating process, loosely bound SO_2 and NO_x are desorbed and transported away in the heating gas stream. The hot gas stream exiting the sorbent heater passes through a cyclone which returns entrained sorbent larger than 20 microns to the top bed. Finally, the hot air is combined with the clean flue gas from the adsorber and the combined streams pass through the baghouse for final particulate removal. Alternatively, the hot air from the sorbent heater may bypass the baghouse and combine with the clean flue gas downstream of the baghouse. The combined streams are then returned to the downstream side of the plant ESP from where the gas will exit the plant stack.

Once the sorbent reaches the regeneration temperature of 1220°F, it is fed by means of a J-valve to the moving bed regenerator. The J-valve is used to both control the solid feed rate to the regenerator and to isolate the sorbent heater from the regenerator. In the regenerator, sorbent is contacted with natural gas in a countercurrent fashion. The off-gases from both sections of the regenerator are then sent to an incinerator where all the sulfur species are oxidized to SO_2. Any excess CH_4 that passes through the regenerator will also be oxidized to CO_2 and H_2O. Both combustion air and natural gas are provided to maintain the incinerator flame. The incinerator exhaust is cooled with air to 1200°F and returned to the power plant duct.

From the steam treatment vessel, the sorbent is again transferred by means of a J-valve to the sorbent cooler. The sorbent cooler is also a three-stage fluidized bed and is also operated in a countercurrent manner. Ambient air passes first through the cooling air blower and then through the three fluid beds. The warm air exiting the cooler is further heated in a natural gas-fired

air heater before being used to heat the sorbent in the sorbent heater. The sorbent temperature is reduced in the cooler to the adsorber bed temperature (248°F) and is then gravity fed to the sorbent surge bin. Finally, by means of another J-valve, the sorbent is fed from the surge bin to the adsorber completing one full cycle.

The POC facility differs from a commercial application of the NOXSO technology in two important areas. First, the POC facility does not include a Claus plant, which in the commercial design would be used to produce a sulfur by-product from the concentrated stream of SO_2 and H_2S produced in the regenerator. This is because Claus technology is commercially available and, therefore, does not require testing at pilot scale. Second, the POC does not include NO_x recycle to the coal combustor. In the commercial design, NO_x in the air leaving the sorbent heater is recycled to the combustor as part of the combustion air. Since NO_x formation in the coal combustor is a reversible reaction, addition of NO_x to the combustion air suppresses the formation of NO_x in the combustor. Since this is an important feature of the NOXSO process, the results of tests on NO_x recycle are presented in this paper. However, NO_x recycle is impractical in the POC test, since the POC treats less than 10 percent of the flue gas produced by Toronto Boiler 10 or 11.

NOXSO PROCESS CHEMISTRY

The NOXSO process chemistry is relatively simple. It involves the chemistry of adsorbing the SO_2 and NO_x pollutants and the chemistry of regenerating the sorbent for reuse using natural gas as shown below.

Adsorption

The NOXSO sorbent consists of $NaAlO_2$ on the surface of a gamma alumina substrate. Sodium aluminate adsorbs SO_2 according to the following reaction mechanism:

$$2NaAlO_2(s) + H_2O(g) \longrightarrow 2NaOH(s) + Al_2O_3(s) \qquad (1)$$
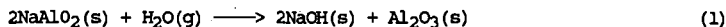
Sodium hydroxide reacts with SO_2 in the flue gas as follows:

$$NaOH(s) + SO_2 \longrightarrow NaHSO_3(s) \qquad (2)$$

The sodium bisulfite is subsequently converted to bisulfate in a reaction with O_2 in the flue gas with NO_x acting as a catalyst.

$$NaHSO_3(s) + 1/2\ O_2(g) \xrightarrow{NO_x} NaHSO_4(s) \qquad (3)$$
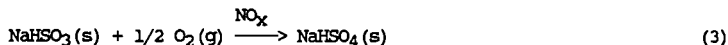
The bisulfate combines with a neighboring active site to form sodium sulfate.

$$NaHSO_4(s) + NaOH(s) \longrightarrow Na_2SO_4(s) + H_2O(g) \qquad (4)$$
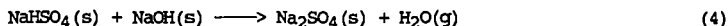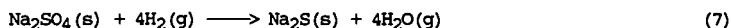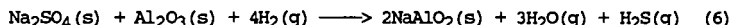
By a similar mechanism, sodium hydroxide adsorbs NO_x from the flue gas to form NaNO2 and NaNO3.

Regeneration

Regeneration is accomplished by heating the spent sorbent in air followed by treatment with a reducing gas. The reducing gas is used solely to reduce sorbed sulfur compounds. Treatment with the reducing gas produces a mixture of sulfur compounds: SO_2, H_2S, and elemental sulfur.

The chemistry of the regeneration step is complex, involving the reduction of sodium-sulfur and alumina-sulfur compounds. Reactions involving the reduction of sodium-sulfur compounds with hydrogen are as follows:

$$Na_2SO_4(s) + Al_2O_3(s) \; H_2(g) \longrightarrow 2NaAlO_2(s) + H_2O(g) + SO_2(g) \qquad (5)$$

$$Na_2SO_4(s) + Al_2O_3(s) + 4H_2(g) \longrightarrow 2NaAlO_2(s) + 3H_2O(g) + H_2S(g) \quad (6)$$

$$Na_2SO_4(s) + 4H_2(g) \longrightarrow Na_2S(s) + 4H_2O(g) \qquad (7)$$

Reaction (7) above produces a sulfide which remains on the sorbent after it has been treated with the reducing gas. In tests to date, the sorbent has been treated with steam, following treatment with the reducing gas, to hydrolyze the sulfide to form H_2S according to reaction (8):

$$Na_2S(s) + Al_2O_3(s) + H_2O(g) \rightleftharpoons 2NaAlO_2(s) + H_2S(g) \qquad (8)$$

The product of NO_x chemisorption, in the case of both the sorbent and the alumina, is unstable at temperatures in the range 350–400°F. Therefore, the sorbent's activity toward NO_x is completely restored as the sorbent is heated to the sulfur regeneration temperature of 1220°F. The sorbent is heated with air in a fluidized bed. The concentrated stream of NO_x in air produced on heating the spent sorbent is recycled to the boiler with the combustion air.

The technical feasibility of returning the NO_x to the combustor was evaluated in two previous pilot tests. The data show that 65 percent and 75 percent of the NO_x returned to the combustor, depending upon the combustor configuration is reduced in the combustor. These tests proved that the technique is feasible although its use will result in a slightly higher equilibrium concentration of NO_x in the flue gas relative to the concentration prior to NO_x recycle.

POC TEST UNIT DESIGN

Adsorber

Internals for the POC adsorber were designed by Dr. Frederick Zenz, a noted expert in the field of fluid bed engineering. The adsorber grid (gas distributor) is a flat perforated plate containing 72,700, 1/16" diameter holes spaced 0.45" center to center on a square pitch. To ensure smooth fluidization, the grid pressure drop was set at 30 percent of the pressure drop across the sorbent bed. The grid pressure drop sets the gas velocity through the grid plate and the grid hole area (given flue gas flow rate). The size of the grid holes is predicated on the observation that holes no larger than four times the particle diameter (d_p = 1409 microns) will not weep on complete shutdown but will inevitably seal off by particle interference or blockage at the lip of the grid hole. A similar approach was used to design the grid plates in the three-staged fluid bed sorbent heater and cooler.

Sorbent is fed to the adsorber through a 6" line entering below bed level and sloped 60° for the horizontal to minimize attrition by minimizing the force of impact as sorbent particles "fall" into the bed. Sorbent leaves the bed by overflow into a 6" downcomer with a detachable section that may be changed to test different bed heights in the adsorber.

Flue gas enters the adsorber at a flow rate of 14,780 ACFM at 233°F. The chemical reactions in the adsorber are exothermic so that the adsorber bed temperature is 250°F. The superficial gas velocity in the adsorber is 2.8 ft/sec, approximately 2.4 times greater than the minimum fluidization velocity and a factor of three less than the terminal velocity of the smallest particle in the bed. At baseline conditions, the sorbent circulation rate is 9,673 pounds per hour into the adsorber. The adsorber settled bed height is two feet, and the sorbent residence time is 45 minutes.

Fluidized Bed Sorbent Heater/Cooler

A fluidized bed is used heat and cool the sorbent because of its extraordinarily effective thermal conductivity. In previous tests, a single stage fluidized bed was used. However, multistaged fluidized beds are preferred since adding more beds increases the efficiency at which the heat in gas and solids is utilized. Energy efficiency was not a primary concern in previous tests. Energy efficiency is a major concern in the POC test, since the POC unit is intended to duplicate the design of the commercial unit.

The fluidized bed internals (i.e., pipes to transport sorbent in and out, standpipes, gas distributor plates, etc.) were designed by Dr. Frederick Zenz in a manner similar to that discussed previously in connection with the fluidized bed adsorber.

Regenerator

Regeneration of the NOXSO sorbent consists of three steps: Heating to 1220°F, contacting with a reducing gas, and contacting with steam. In the first step, heating the sorbent, adsorbed NO_x is desorbed from the sorbent surface. Measurements made during the LCTU tests show that from 76 percent to 99 percent of the adsorbed NO_x was detected in the sorbent heater offgas. Within limits of measurement error, this represents complete regeneration of the sorbent with respect to NO_x.

Besides NO_x, some adsorbed SO_2 is released in the sorbent heater. Based on LCTU results, from 2.2 percent to 8.6 percent of the adsorbed SO_2 was detected in the sorbent heater offgas stream with an average of 6 percent.

After reaching the regeneration temperature of 1220°F, the sorbent is transferred from the sorbent heater to the moving bed regenerator. The adsorbed sulfur compounds are regenerated by contacting the sorbent with a reducing gas followed by steam. During the three completed test programs, H_2, CO, H_2 + CO, H_2S, and natural gas were used as the reducing gas. The offgas from the regenerator contains SO_2, H_2S, and elemental sulfur with the relative proportions dependent on the reducing gas used.

Each of the reducing gases, when coupled with steam treatment, successfully regenerated the sorbent. Natural gas required a higher temperature for regeneration (1130°F) compared to H_2 (1050°F) or H_2S (950°F). Nonetheless, natural gas was chosen as the regenerant for the POC based on economic considerations, availability, and the fact that natural gas generates the most favorable product mix for a Claus plant feed.

Sorbent residence times were determined from laboratory experiments performed at W. R. Grace and NOXSO using methane followed by steam to regenerate the sorbent in a fixed-bed reactor. The required sorbent contacting time with reducing gas was found to be 30 minutes and with steam 20 minutes. With residence time and sorbent circulation rate fixed, the regenerator inventory and hence volume can be calculated according to:

$$V = I/\rho = W(RT_s)/\rho$$

where
V = sorbent volume, ft^3
I = sorbent inventory, lbs
ρ = sorbent bulk density, lb/ft^3
W = sorbent circulation rate, lb/hr
RT_s = sorbent residence time in regenerator, hr

THE POC regenerator consists of two distinct moving bed reactors encased in a single, cylindrical shell, four feet in diameter and approximately 40 feet high. (Note: The POC regenerator is intentionally sized larger than required to allow testing of sorbent circulation rates and residence times beyond the range of baseline conditions.) Sorbent moves through the upper section of the regenerator and into a conical section which separates the natural gas and steam treatment sections of the reactor. To guard against "rat-holing," i.e., sorbent moving through the center of the reactor faster than along the walls, the angle of the cone is 70° which is greater than the sorbent's angle of internal friction. Natural gas in fed into the conical section through a series of concentric rings hung inside the cone. The rings provide a gas space between the moving bed of sorbent and the reactor wall and serve to distribute the gas within the bed.

The rings are placed at an angle of 45° to the horizontal. The sorbent's angle of repose is 23°. Sorbent leaving the upper section of the regenerator passes through a six-inch pipe into the steam treatment section. The steam treatment section is also a cylindrical vessel with a 70° cone at the bottom. Steam is fed into the cone through a series of rings identical to those in the upper section of the regenerator.

The POC will use a dense phase lift to convey the sorbent and no valves will open or close on the sorbent.

The transport system will be a dense phase pneumatic lift that should be much less attriting than the conveying system used in previous tests. The attrition rate of 0.03 percent/hr of the fluid bed inventory gives an attrition rate at the POC of about 6 lbs/hr at base case conditions.

PROCESS SUMMARY

The NOXSO process has the following operating advantages over both existing and developing sulfur removal processes:

* Simultaneous removal of SO_2 and NO_x in a single reaction vessel.

* Produces no secondary pollution in the form of solid or liquid waste.

* Applicable to all coal types and sulfur contents.

* Completely dry process with no need for stack gas reheat.

* Cost effective when compared to conventional technology, i.e., flue gas desulfurization plus selective catalytic reduction.

* Applicable to new and retrofit installations

Figure 1
Proof-of-Concept Process Flow Diagram

Legend:
1. Flue gas fan
2. Flue gas spray cooler
3. Fluid bed adsorber
4. Cyclone
5. Baghouse
6. Sorbent makeup bin
7. Pneumatic transport receiving hopper
8. Regenerator
9. Fluid bed sorbent cooler
10. Fluid bed sorbent heater
11. Air heater
12. Sorbent surge bin
13. Cooling air fan
14. Incinerator

1462